THE APPARENT FORCES BETWEEN FINE SOLID PARTICLES TOTALLY IMMERSED IN LIQUIDS

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BY

W. J. A. BLISS

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THE APPARENT FORCES BETWEEN FINE SOLID PARTICLES TOTALLY IMMERSED IN LIQUIDS. I.

By W. J. A. Bliss.

THIS investigation was undertaken at the suggestion of Professor Milton Whitney, of the United States Agricultural Department, in order to throw light on the physical bearings of certain points in his theory of the effect of fertilizers upon the retentiveness of soils for moisture. I desire to express my obligations to him for his continual interest and valuable suggestions, and for much information and many references upon the subject of flocculation.

I would also acknowledge my indebtedness to Professor Rowland for his courtesy and assistance at all times; and to Dr. Joseph S. Ames for his continual guidance and suggestions in both theory and experiment.

§ 1. The experiments described in the first part of this paper were made in order to reproduce, if possible, some of the phenomena of flocculation under more definite and controllable conditions, while in the second part (to be published in a subsequent number of the Physical Review) an attempt is made to give a fuller theory of these phenomena than has hitherto appeared. The facts of flocculation are well known and may be summarized as follows: —

When a few drops of various solutions are added to a jar of pure water, in which clay or finely divided sand is suspended, certain marked effects occur: —

(1) If acids, lime, common salt, or almost any acid or neutral salt are added, the clay particles gather themselves into groups, — they become flocculated.

(2) When a very small trace of ammonia, caustic potash or soda, carbonate of potash or soda, or borax is added, the particles seem to attain a more finely subdivided condition than in pure water and may thus be held in suspension much longer.

(3) When an excess of these last substances is added, the same effect is produced as by the addition of acids, — flocculation is caused.

PART I. EXPERIMENTS.

§ 2. Observations on flocculation have, for the most part, been made only incidentally in experimenting upon the rate of settling of sediments in water and solutions. Professor Whitney has, however, placed a little clay-water under a powerful microscope, and upon adding a drop of very dilute hydrochloric acid has seen the particles form into closer groups. Violent currents are, of course, set up by the entry of the drop, so that individual grains can hardly be watched and little can be told of the process which has taken place except that, after the currents cease, the grains are in groups instead of separate.

§ 3. It therefore seemed interesting to try with larger bodies, whose movements could be more closely watched, whether the film of liquid, which we must suppose to be adherent to each of their surfaces — even when in so-called contact under water — could be made to change its thickness considerably by adding a slight trace of salt, and whether a sufficient force could be so called into play to move the bodies. This is, of course, a totally distinct phenomenon from the well-known interactions of floating solids, such as corks, though both are due to the same molecular forces. Experiments were accordingly begun in November, 1892, by a method suggested by Dr. Ames. A pair of large lenses, used for projecting Newton's rings in lecture experiments, were

placed one on top of the other in a vessel of pure water, and the reflected system of rings obtained. Several grams of 20 per cent salt solution were then put in. A simultaneous expansion of the rings would have meant that the glasses had moved nearer than in pure water, a contraction the reverse, but the lenses were far too heavy, and no motion could be observed even with a microscope. After several months of trial of more and more delicate modifications of this apparatus, the following method was found to answer: —

Method.

§ 4. *ABC* (Fig. 1) is a large evaporating crystal which was filled with pure water and placed under the microscope. *L* is an ordinary spectacle lens and *F* a very small fragment of a microscope cover-glass, the thinnest obtainable. A mirror reflected a

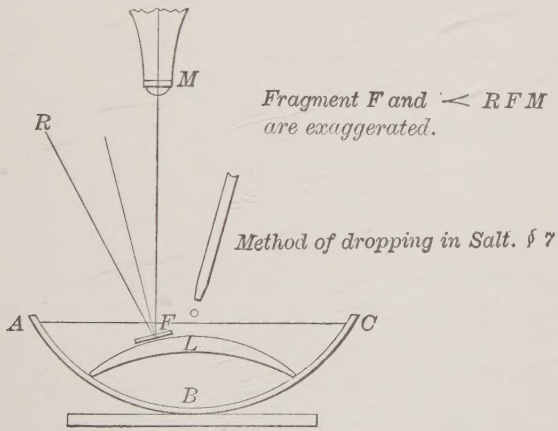


Fig. 1.

beam of sodium light *RF* on this fragment, and the Newton's rings formed between its lower surface and the lens were observed in a microscope *M*. The latter was fitted with a three-inch objective and a micrometer, whose scale was 1 mm. = 675 divisions. An average size of the fragment of cover-glass used was 400 × 600 divisions, or about one-half a square millimeter in area, weighing $\frac{1}{4}$ mg. The appearance of the rings was now carefully noted,

and their position determined with the micrometer cross-hairs. After watching carefully for half an hour or more to make sure that no accidental change was taking place in the rings, a little solution of the salt to be tried was introduced, the manner varying as the experiments gave more experience. Whether the light fragment had been attracted closer to the surface of the lens or repelled from it was now shown by the way the rings changed. The amount even of motion away from the lens could be roughly determined by the number of times the central spot changed color, the surrounding rings meanwhile shrinking. On the other hand, an expansion of the rings denoted a drawing down of the fragment, and the distance could be approximated in the same way. Further details will be found in §§ 7 to 10 below, and a consideration of the effect of change in the index of refraction and other sources of error in § 11 and § 12.

Results.

§ 5. The substances tested were:—

(1) NaCl and HCl (chiefly the former), as types of substances which tend to produce flocculation.

(2) KOH and NH_4OH, as types of those which tend to prevent it.

§ 6. The results are briefly:—

1. KOH. (*a*) The first effect of the change from pure water to very dilute KOH is to raise the fragment, off the lens, very roughly a distance of 7×10^{-5} cm. on the average.

(*b*) As the solution around the fragment grows in strength, the direction of motion is reversed, and the fragment settles back partly. This return motion did not always take place, and when it did, was usually less than the direct, so that the fragment was left further from the lens than in pure water.

(*c*) By increasing considerably the amount of KOH by further additions, the fragment was sometimes brought back to its position in pure water, and, more rarely, seemed to be drawn closer to the lens.

(*d*) By Method I., which allowed the solution about the particle of cover-glass to decrease in density as the salt first added settled

to the bottom, the fragment would be drawn down when a second drop was added, would rise again as this in turn settled, and could be made to repeat this process several times, approaching, however, a position closer to the lens as the repeated drops began to affect the strength of the solution throughout the vessel.

(*e*) By Method II., which allowed solution of definite density gradually to replace pure water, .0007 gr. per cubic centimeter was shown to be too much KOH to produce the greatest separation of lens and fragment. .0024 seems to be enough to bring them closer together than in pure water, though this limit is more uncertain.

To sum up: A trace of KOH — less than .0007 gr. per cubic centimeter — added to pure water tends to increase the thickness of the glass-liquid surface film and so separate two glass surfaces immersed in the liquid. An excess beyond this trace tends to reverse this phenomenon. (Compare effects of excess of alkali on suspended clay or sand particles § 1.)

2. NH_4OH. Few experiments were tried with this substance on account of the fumes. Of four experiments, one gave no result, one a drawing down of the fragment (flocculation), two (one of them very accurate) a result precisely like KOH.

3. NaCl. A large number of trials were made with this, most of which showed absolutely no motion of the rings. A few of the earlier experiments gave contradictory motions one way or the other. The later, more careful ones showed either no change whatever or, in one or two instances, a motion of as much as 1×10^{-5} cm. towards the lens, so small a distance that it may easily have been imagined or due to accident.

4. HCl. Tried only a very few times, usually without effect. Once there seemed to be undoubted raising of the fragment, once a slight drawing down, and once a raising followed, with increasing strength of solution, by a greater drawing down.

In a number of experiments after repeated failure with drops of NaCl and HCl, a drop of KOH on being added at once produced its characteristic effect. This indicates conclusively that the effects of KOH are not due to currents in the liquid, since the solutions were all dropped in in the same way and were, moreover, very closely of the same density and index of refraction.

Borax was tried once without result.

Details.

§ 7. The chief difficulty to be overcome was in making the change from pure water to dilute solution. At first a much larger vessel than that described in § 4 was used, and the salt was added by pouring in a few grams of 20 per cent solution at a distance from the fragment. The time taken for the solution to reach any given strength around the fragment was indeterminate, and therefore the position of the rings had to be observed with great care from the moment the salt was put in until all possibility of effect was past. This was done by making, during this time, repeated settings of the cross-hairs upon the middles of three or four successive bands, which could be done to within $\frac{1}{20}$ of the width of a band. In the course of from five minutes to an hour or more from the time of putting in the salt, there were at times considerable changes in the positions of the rings, *i.e.* a shifting in or out of $\frac{1}{4}$ or $\frac{1}{2}$ the width of a ring. There was, however, never any certainty that the changes were coincident with the arrival of the salt in the neighborhood of the fragment, and the results could never be repeated with any certainty by trying to reproduce the same conditions. It may, however, be said that observations kept up for an hour before any salt was put in rarely showed a small fraction of the change which followed its addition. The results as a whole were, however, contradictory and showed nothing.

The shallow crystal shown in Fig. 1 was now substituted for the larger vessel used before, so that a drop of solution could be put in with a rod or dropper, as in that figure, and settling to the surface of the lens, pass over the spot occupied by the fragment. It was then easy to ensure the presence of salt in the surface films between the two within a few minutes after the drop was put in by giving the lens a very slight slope and dropping in the solution a little higher up than where the small fragment F lay. The whole process was now as follows: —

METHOD I. — The lens, dish, and a number of fragments were soaked for a day in strong bichromate solution. They were then carefully washed in running water and left to soak in it over night. With a final rinsing in the morning in water filtered to

remove grit, the fragments were picked up on a glass rod and placed on the lens, care being taken to touch the latter only on the edges. The lens was then put in the dish and a final rinse given. This was sure to wash the light fragments off the lens if the surfaces were not so clean as to make very good contact, and therefore furnished a very useful though often most provoking test of the efficiency of the cleaning process. Enough filtered tap-water was now put in to cover the lens entirely, and the whole put under the microscope. The reflector was then placed so as to make the angle *RFM* as small as possible. All the fragments were then brought into the field in turn, and the one which gave the most perfect rings chosen. The position of one or more of the edges of this were then fixed with the micrometer as a check upon motion of the fragment as a whole along the lens. A rough sketch of the fragment and a few of the central rings being made, and also a note descriptive of the general appearance of the whole system of rings, the latter were carefully watched for a half hour, and, if any change occurred in their position or in the point of closest contact between the fragment and lens, the former was discarded as not trustworthy, and others successively were tried until one was found that stood the test. A drop of solution — 20 per cent in the earlier and 5 per cent in the later experiments — was now put in, as described above, and in the course of a few minutes the changes in the rings took place, whenever there were any at all. These were carefully noted, together with the time at which they took place, and were afterwards tabulated, so that the whole evidence could be seen together. Extracts from these tables are given herewith.

TABLE I.

METHOD I.

(+ means motion of rings *out*, or glass *down*.)

No.	Solution and number of drops.	Motion.		Remarks.
		Rings (number of changes).	Fragment (10^{-5} cm., up and down).	
XXIII.	KOH 20% few drops	−10 then reversed +2	−30 +6	Rings very good and complete. Size of fragment, 3 sq. mm. Both same in XXV. and XXVI.
	NaCl 20% repeated drops	No effect at all		Nos. XXIII.–XXVIII. contrast the effect of acid and alkali, no change whatever being made between the two parts of the experiment.
XXV.	HCl several	No effect		See No. XXIII.
	KOH 20% 1 or 2	Marked contraction		
XXVI.	several each of NaCl & HCl	No effect with either		See No. XXIII.
	KOH 20% 1 or 2	Marked contraction		
XXVIII.	NaCl 20% several	$+\frac{1}{2}$ −5	+1.5 −20	Very small fragment, .2 mm. in area, triangular in shape, with point of contact in one corner. About 60 of rings showing. See, also, XXIII.
	KOH 20% 3 or 4	−5	−15	
XXXV.	KOH Very dilute few drops	−1 followed by	−3 *greater* +	Washed in HCl instead of bichromate. One of very few experiments where reverse motion was greater than the original.

TABLE I. (*continued*).

METHOD I.

(+ means motion of the rings *out*, or glass *down*.)

No.	Solution and number of drops.	Motion.		Remarks.
		Rings (number of changes).	Fragment (10^{-5} cm. up and down).	
XXXI.	NH_4OH dilute	−1	−3	Showing effect of excess of alkali, as do also XXXVII. and XXXVIII. Rings clear and complete. Fragment large, about 4 sq. mm. Each time a drop of KOH entered, it drew down the fragment, which rose as the salt settled or became diffused, but not to so great a distance from the lens as before. Hence, as the solution throughout the vessel strengthened, the change each time became less, and the fragment drew continually nearer to the lens.
	1 or 2	followed by		
		+½	+1.5	
	more	−1¼	−3.7 .	
		(no reverse motion)		
	KOH 20 %	+6	+18	
	1 or 2	followed by		
		−5	−15	
	1 or 2 more repeated	smaller + smaller −	followed by each time	
XXXVII.	KOH 20 % 1 drop	−1½	−4.5	Washed in very strong bichromate solution for 3 hours and then in running water for 2, and obtained very clear and steady rings.
	several more	no effect		
	more yet	+1.5	+4.5	
		followed by		
		−¼	−3.8	
	twice again	each time the last growing less	same as	
XXXVIII.	KOH 5 % 1 drop	−2.5	−7.5	First experiment after four months' absence. Very much like the last, except that the fragment does not seem to have risen between the last drops.
		followed by		
		+1.7	+5.0	
	more	+½	+1.5	
	more	no effect		

§ 8. After the preliminary methods had been given up, all the experiments, except six with KOH, were made substantially as above. Not one single instance of a contraction of the rings following the addition of NaCl was observed by this method, and most of these experiments were never even tabulated. Of six that are included in the table, three show no motion whatever, and three a very slight spreading of the rings, the greatest amount being one-half the width of the central spot, *i.e.* corresponding to an approximation of the two surfaces by 1.5×10^{-5} cm. This lack of effect is easily explained on the theory that NaCl would, if possible, produce a drawing together of the surfaces, as it flocculates clay; but they could actually move closer only in a few accidental cases, since the weight of the fragment, of itself, pressed it into contact with the lens, owing to the care which was taken to have the surfaces perfectly clean. With KOH, on the other hand, within a very few minutes after the drop went in, the rings would almost invariably draw in towards the center, the latter changing color about four times on the average. This change occupied about one-half minute, and was then often followed by an immediate reversal of the motion of the rings. This reverse motion was sometimes rapid, at times quite gradual, but very rarely did it indicate a motion beyond the point from which the fragment originally started. Sometimes it took a dozen drops to bring the fragment as close to the lens as it would go, and in the meanwhile each drop, as it entered, would draw it down, and in five or ten minutes it would commence to rise once more as the drop flowed past and solution around the fragment weakened, only to be again drawn down a little further by the entry of the next drop, thus indicating that for each degree of the strength of solution there was a tendency to a film of liquid of definite thickness between the glasses.

The trials with HCl and NH_4OH need not be dwelt upon, as, where any results followed, they were like those with NaCl and KOH. The most interesting experiments by this method were those where a number of drops of NaCl (or in two experiments HCl) were added and produced no effect, or, in a few instances, a slight approximation of the glasses; and then, without in any

manner changing the position of the little fragment or any other condition of the experiment, a drop of KOH was put in, and found at once to produce its characteristic separation of the glasses. It was thus shown very conclusively that the effects with this salt were in no way accidental, but depended on a specific difference between it and the two others, since the drops were all put in in the same manner, and were carefully made of very nearly the same refractive index. Moreover, by reversing the process and adding the alkali first, the same difference was shown.

§ 9. Method II. — To show more conclusively that the effect of KOH was not due to disturbance on account of currents in the liquid, and to gain, if possible, a more definite idea of the density of the solution which accompanied the phenomena, the following more elaborate method was used a few times, only with KOH :—

The lens was supported near the top of a much deeper vessel, into the bottom of which liquid could be introduced by a siphon from a glass reservoir. The latter was supported on a stand of variable height, so that the rapidity of the flow through the siphon could be regulated or even reversed if necessary. The vessel containing the lens being placed under the microscope, the siphon was started and the vessel filled. The flow was then stopped, and the best fragment, as to rings and stability, was selected by trial as before, and the flow of water being again started, was watched for half an hour or more to test the effect of the mere current upwards due to the siphon, which was run at a considerably greater rate than that afterwards used. If, as was usually the case, the fragment was found to be so stable that the rings were in no degree affected by this much more rapid flow, the reservoir was filled with water to a known mark and a measured quantity of the KOH solution stirred into it. Now starting the flow at a very slow rate, the salt solution of known concentration very gradually rose in the vessel under the microscope, the pure water flowing off at the top. The fragment was always so placed that it would be directly under the point of overflow, so that the alkalinity of the liquid in which it lay could be easily determined by touching test paper to this overflow. In this manner the

moment when the liquid at the point in question changed from pure water to solution of known strength could be ascertained very closely. Its very remarkable coincidence with the time of the changes in the rings in the few trials made by this method, served to preclude any doubt that one was the cause of the other, while the almost imperceptible strength of current prevented the phenomena from being ascribed to such mechanical disturbance. These experiments gave, further, the rough values of the respective strengths of solution which caused the greatest separation of the two surfaces and a closer approximation than in pure water. These were given in § 6.

TABLE II.

METHOD II. (BY SIPHON.)

(+ means motion of the rings *out*, or fragment *down*.)

No.	Grams KOH per cu. cm. siphoned in.	Motion.		Remarks.
		Rings (number of changes).	Fragment (10^{-5} cm. up and down).	
XLII.	.0024	+2.5	+7.5	No contraction at all; fragment seems suddenly to have passed from the pure water into solution dense enough to show effects of excess of alkali. See section 10 and Fig. 2.
XLVI.	.0008	−2	−6	Washed in fresh bichromate. Center of rings shifted a very little, otherwise experiment was very good. After the first part of the experiment the .0008 solution was run off and siphon filled with the stronger solution.
		followed by		
		+1.5	+4.5	
	.0015	slight further +		
XLVII.	.0007	−1.5	−4.5	Made to test the effect of acidity or alkalinity of surface before experiment. Everything precisely the same as in XLII. except that between the two the lens and fragments were soaked in strong KOH and then in running water.
		followed by		
		+5	+1.5	

§ 10. The way in which observations of changes in the rings were usually noted is shown by the sketches in Fig. 2, which are copied from my note-book, Experiment No. XLII. The shape of the fragment was a trifle more irregular, but roughly a triangle in which $AB = .89$ mm., $AC = 1.42$, $BC = 1.54$. The same ring is made heavy throughout and serves to fix the amount and direction of the change in the whole system. The siphon ran at varying

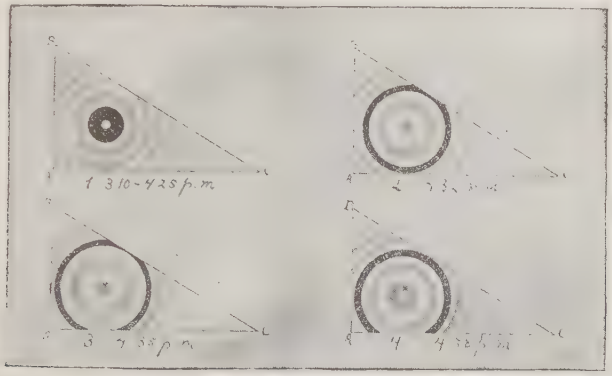


Fig. 2.

rates with pure water (Method II. was used) from 2.45 P.M. to 3.25, and was then started with KOH solution whose strength was .0024 grams per cubic centimeter. The change noted in sketch 2 began at 4.25. An expansion from the center of two rings is shown, as also that the stability of the fragment was not very good, since it tilted over a very little towards AC during the experiment.

In the earlier experiments distilled water was used, but it was found that that available was a little greasy, and in all the later trials filtered tap-water was used for the final washing and the experiment itself. .

Sources of Error.

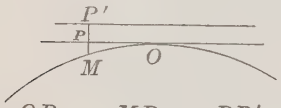
§ 11. Change in the Index of Refraction. — Let the point P (Fig. 3), in a plane tangent at O to a sphere of radius R, be at a distance $MP = e$, from the sphere, measured perpendicular

to the plane; and let $OP = \rho$. Then if P' is a point in a parallel plane at a distance p above the tangent one, $t = p + e = MP'$.

$$\text{Hence} \qquad \rho^2 = 2Re = 2R(t - p) = \left(\frac{n}{2\mu}\sec. r - 2m\right)\lambda R, \qquad (1)$$

where λ is the wave-length in air; r the angle of refraction through the film of liquid, and μ the index of refraction of the latter; and where $m = \frac{p}{\lambda}$, *i.e.* m is the distance p expressed in wave-lengths in air. n is the number of the ring of radius ρ from the center and is, of course, even for a dark band and odd for a light one.

The point observed in the experiments was the number of times the central spot ($\rho = 0$ approximately) changed through a complete cycle, *i.e.* from n to $n-2$, n being always counted from the ultimate black spot which would occupy the center were the lens and fragment in perfect contact. If, then, n changes from n to $n + \delta$ when salt is put in and the index of the dilute solution thus formed is μ_1, then the condition that it is the central spot which is being observed gives



$OP = p.$ $MP = e$ $PP' = p.$
$MP' = t.$
Fig. 3.

$$\frac{n}{2\mu}\sec r - 2m = \frac{n+\delta}{2\mu_1}\sec r - 2m_1 = 0,$$

or

$$m_1 = \frac{\mu}{\mu_1}m + \frac{\sec r \cdot \delta}{4\mu_1}.$$

Therefore, if

$$\frac{\mu}{\mu_1}m + \frac{\sec r \cdot \delta}{4\mu_1} > m\,; \text{ i.e. } \frac{\sec r \cdot \delta}{4} > m(\mu_1 - \mu),$$

m_1 is greater than m, *i.e.* the particle has moved away from the lens. In order, then, that the change δ shall be wholly accounted for by the change in the index of refraction, m, the distance of the fragment from the lens at starting must be at least as great as

$$m = \frac{\sec r \cdot \delta}{4(\mu_1 - \mu)}.$$

I give below the requisite values of m for various values of δ, the number of times the center changed color. The data are for 5 per cent and 20 per cent solutions, the strength of the *drops* put in, which was very much diluted before reaching the fragment, and for $r = 0$, which makes m a minimum.

	μ_1.	$\mu_1 - \mu$.	m		
			$\delta = 1$.	$\delta = 2$.	$\delta = 4$.
NaCl 5 %	1.340	0.006	41	83	167
20 %	1.369	0.035	7	14	29
KOH 5 %	1.341	0.007	35	71	142
20 %	1.360	0.026	9	19	39
NH_4OH	—	negative	∞	∞	∞

The average change in the experiments due to a few drops of 5 per cent KOH was a contraction of two rings ($\delta = 4$), and to account for it wholly we should have to suppose a distance of 142 wave-lengths or $\frac{1}{10}$ mm. to separate the two glass surfaces supposed to be in contact at starting. Further, the change in the rings with NaCl should have been greater than with KOH; and NH_4OH should have produced the opposite change to what it did. The indices for such dilute solutions are not given in Landolt and Börnstein's tables, but were calculated from refraction equivalents. They are at 18° and μ for water is taken as 1.334.

§ 12. Osmotic Pressure. — A more important source of error was suggested by Dr. Ames, who thought there might be a very strong force tending to lift the fragment due to imperfect diffusion of the salt into the interstice between the two glasses. A method of attacking the question was found in an extension of an equation given by J. J. Thomson.[1] The Lagrangian function of the molecules of salt (supposed to behave like those of a perfect gas) in the volume of a solution and also in the surface films bounding it, is there given. Here two similar terms were added for the volume of liquid between the glasses and the two glass surfaces bounding thereon, the density of the salt being supposed to differ there from

[1] Application of Dynamics to Physics and Chemistry, pp. 190, ff.

its value in the open liquid immediately around. The glass surfaces are for simplicity assumed plane and parallel and separated by a distance x. If, then, H is the Lagrangian function of the salt molecules in the interstice and the liquid immediately around the fragment, $\frac{\delta H}{\delta x}=F$ is the force tending to separate the two. To determine F completely would require a knowledge of the rate at which the solutions become equalized in strength as x increases under the action of the force. A minimum value, not far from the true one, may be found by assuming that the only change is that due to the flow into the interstice, as the particle rises, of enough strong solution from without to fill the increase of volume.

Let v_1 represent the volume of liquid between the fragment and the lens; $\frac{1}{2}S_1$, the area of the lower face of the fragment, *i.e.* S_1 the total area of glass surface bounding the volume v_1; t_1 the thickness of the film on this surface and T_1 its surface tension, ρ_1 and σ_1 the densities of salt in v_1 and S_1 respectively; and $\eta_1=v_1\rho_1$ and $\xi_1=\sigma_1 S_1 t_1$ the total weights of salt in each. Let the same characters without subscripts denote similar quantities in the liquid immediately around. J. J. Thomson's equation for H is (adding two necessary terms in the subscript quantities):—

$$(1)\qquad H=\eta R\theta\log\frac{v\rho_0}{\eta}+\eta\{f(\theta)-\omega_1\}-ST$$
$$+\eta_1 R\theta\log\frac{v_1\rho_0}{\eta_1}+\eta_1\{f(\theta)-\omega_1\}-S_1T_1$$
$$+\xi R\theta\log\frac{St\rho_0}{\xi}+\xi\{f(\theta)-\omega_1\}$$
$$+\xi_1 R\theta\log\frac{S_1t_1\rho_0}{\xi_1}+\xi_1\{f(\theta)-\omega_1\};$$

where θ is the temperature and R an analogous quantity to the same symbol in Thermodynamics, *i.e.* $R\theta\rho=p$, the osmotic pressure; ω_1 and ρ_0 are constants of integration not depending on x. Remembering that

$$(2)\qquad \frac{\delta\eta}{\delta x}+\frac{\delta\eta_1}{\delta x}+\frac{\delta\xi}{\delta x}+\frac{\delta\xi_1}{\delta x}=0;$$

since the total quantity of salt is not a function of x, we get

$$F=\frac{\delta H}{\delta x}=R\theta\left[\left\{\frac{\delta\eta_1}{\delta x}+\frac{\delta\xi_1}{\delta x}\right\}\log\frac{\rho}{\rho_1}-\tfrac{1}{2}S_1(\rho-\rho_1)\right].$$

For complete solution we need an equation giving

$$\frac{\delta\eta_1}{\delta x}+\frac{\delta\xi_1}{dx},$$

the rate of inflow of salt as the fragment rises, but we can find a minimum by assuming that no diffusion takes place during the very short time occupied by the change in the rings, and no weak solution flows out to be replaced by stronger. Then

$$\frac{\delta\eta_1}{\delta x}+\frac{\delta\xi_1}{\delta x}=\rho\frac{\delta v'_1}{\delta x}=\tfrac{1}{2}\rho S_1,$$

since $\frac{1}{2}S_1$ is the area and x the height of the space v_1. Substituting we get the minimum value of the force,

$$F=\frac{R\theta}{2}\left[S_1\left\{\rho\left(\log\frac{\rho}{\rho_1}-1\right)+\rho_1\right\}\right].$$

Remembering that $p=R\theta\rho$, we have

$$F'=\frac{S_1}{2}\left\{p\left(\log\frac{\rho}{\rho_1}-1\right)+p_1\right\},$$

where S_1 is the area of glass bounding on the interstice, *i.e.* twice the area of the lower surface of the little piece of cover-slip; ρ_1 is the density of salt in the interstice and ρ in the liquid outside; and p_1 and p are the pressures of a number of hydrogen molecules per unit volume equal to the number of salt molecules in densities given. The assumption that the salt in dilute solution follows Avogadro's law is to be noted. From data in Everett's "C. G. S. System of Units," $p=4\times10^8\rho$ and $p_1=4\times10^8\rho_1$. Hence

$$F'=2\times10^8S_1\left\{\rho\left(\log\frac{\rho}{\rho_1}-1\right)+p_1\right\}\text{ dynes,}$$

or

$$4\times10^6\rho\left\{\frac{\rho_1}{\rho}-\left(1+\log\frac{\rho_1}{\rho}\right)\right\}$$

dynes per square millimeter of the under surface of the glass fragment. In the following table F' is given for various ratios of

the density in the interstice to that in the liquid around. ρ is taken as .00075, an average value in the experiments by Method II., where alone the density was definitely known.

F' FOR KOH.

$\frac{\rho_1}{\rho}$.	F'.	$\frac{\rho_1}{\rho}$.	F'.	$\frac{\rho_1}{\rho}$.	F'.
0.00	∞	0.10	4200	0.70	180
0.01	10830	0.30	1500	0.90	15.7
0.05	6150	0.50	520	1.00	00

In order to compare this with the force downward due to the weight of the fragment, a whole cover-slip was weighed and its diameter measured, and was found to weigh .46 mg. per square millimeter, or to be subject to a downward force of 2.94 dynes per square millimeter in water, which is insignificant compared to F'.

Considering the first effect with KOH alone, *i.e.* the rise of the fragment as the drop of solution reaches it, this force would abundantly explain the action, since the fragment ought to rise until the densities above and below it became equal, and then, the force having ceased to exist, drop back. The explanation is insufficient because: —

(1) Were this force alone acting, a second drop should again cause the fragment to rise, since the solution beneath it would again be more dilute than that outside, but in the majority of cases the reverse was the case and a second drop, if it produced any effect, usually caused a fall of the fragment, which is quite in accord with the fact that excess of alkali flocculates.

(2) So far as could be found,[1] NaCl, in ordinary cases, diffuses less rapidly than KOH, and if this holds for very dilute solutions and capillary openings, we should expect a greater disparity in the strength inside the interstice and without in the case of NaCl, and consequently a greater lifting force, whereas no lifting at all was observed. The lifting force for equal ratio of the strength inside and out is with NaCl 95 per cent of that with KOH.

[1] Ostwald's Solutions, trans. by Muir, p. 134.

While, in the absence of sufficient data with regard to diffusion in capillary spaces, some may prefer to consider the experiments as largely explained by the osmotic force, it seems to the writer more natural to suppose, considering both (1) and (2), that the effects are the result of two sets of forces both tending to raise the fragment in the case of dilute KOH, and, on the other hand, almost exactly counterbalancing each other in the case of NaCl and stronger KOH, the first set being the molecular forces which act in flocculation, and the other those which bring about diffusion.

§ 13. To sum up: The effects summarized in § 6 are a reproduction of those observed in the flocculation of clay particles, as may be seen from the following comparison: —

Results of the Experiments.	*Flocculation.*
1. The effect of very dilute alkalies, represented by KOH, is to raise the glass fragment away from the lens.	1. Fine solid particles are held further apart in very dilute alkaline solutions than in pure water.
2. As the KOH solution became stronger the fragment returned to its original position, and at times seemed drawn closer to the lens.	2. More concentrated alkaline solutions reverse this effect and cause flocculation.
3. If the glass surfaces were closely in contact at starting, very little effect should have been expected from substances tending to draw them closer. They could only act by bending the fragment. This lack of effect was found with NaCl, in marked contrast with the strong effect of KOH.	3. The effect of NaCl and the other substances of its class is to produce a closer grouping of the particles of clay than in pure water.

The writer hopes to extend these qualitative results to a wider range of substances and, if possible, obtain quantitative observations connecting the thickness of the adherent films separating the glasses with the density of the solution.

THE APPARENT FORCES BETWEEN FINE SOLID PARTICLES TOTALLY IMMERSED IN LIQUIDS. II.

By W. J. A. Bliss.

Part II. Theoretical.

§ 14. In Part I. the phenomena of flocculation have been shown to be capable of close reproduction between two pieces of glass, at least so far as the effect of KOH is concerned. The evidence in the case of NaCl is indirect, but still strong. As these two substances are typical of the two classes as to effect on flocculation, these experiments furnish a very conclusive argument in favor of a purely physical explanation of the phenomena in question, rather than the one usually opposed to it, that there is a chemical change, at least in the coating, of the flocculated particles. The following discussion of the manner in which such phenomena might result from molecular forces may be divided into five heads: —

(1) Previous state of the theory. Sections 15–17.

(2) Proof that the force which tends to hold two submerged particles apart may be considered to be proportional to the difference between the coefficients of molecular force between a unit volume of solid and a unit volume of liquid, on the one hand, and two unit volumes of liquid on the other. Sections 18 and 19.

(3) Expression of these coefficients in terms of the densities of the solid, liquid, and salt in solution, and the constants of attraction between unit masses of these substances. Sections 20–23.

(4) Rough determination of the relative magnitudes which it is necessary to assign to these last constants in order to explain the phenomena of flocculation. Sections 24–27.

(5) Suggestions as to further investigations along these lines. Section 28.

§ 15. Barus[1] has advanced as a possible factor in a physical explanation, that the bombardment of two particles by the molecules of salt in solution forces them together in a manner similar to Lesage's theory of gravitation. This explanation is supported by the close resemblance between the order of substances in producing flocculation and their order as to electrolytic conductivity,[2] which suggests that both might alike depend on the number of ions. It fails to explain, however, the action of alkalies, since it would be difficult to suppose that in this case the ions were more active between the particles and so produced a repulsion.

§ 16. More probable explanations are those based upon the molecular forces between solid-and-solid, liquid-and-liquid, solid-and-liquid. Barus[3] suggests that the size of a particle of precipitate depends on these forces, the first two aiding, the other opposing, its growth. There is then a critical size, which determines the coarseness of the precipitate. Barus and Schneider[4] suppose each particle surrounded by an adherent envelope of liquid. The thickness of this shell depends upon the intensity of the attraction between solid and liquid. If the shells are large or the number of particles great, the latter cannot gather together or settle in a mass to the bottom without parting from these adherent envelopes. The shells must then shrink before flocculation or settling can take place. Such shrinkage is brought about by a decrease in the attraction between solid and liquid, due to rise in temperature; by the drawing together of the liquid molecules in freezing; or by a portion of the shell leaving the particles to adhere to salt molecules when such are introduced. Any of these causes should aid flocculation, as they actually do. Bodländer, in the paper already mentioned, has a similar but vaguer explanation.

§ 17. The most complete theory the writer has found is that of

[1] Bull. 36, U. S. Geol. Surv.

[2] Barus, *loc. cit.*, and also Am. Jour. Sci., February, 1889. Also, Bodländer, Gött. Nach., 1893, pp. 267–276.

[3] Barus, *loc. cit.*, p. 127.

[4] Zeitschrift für Phys. Chemie, VIII. 3, 1891, p. 290.

Professor Milton Whitney.[1] As variously stated in treatises on surface tension, if AB is the surface of separation of a liquid and some other substance, a molecule at P, Fig. 4, has a different potential from a molecule at Q, the circles about these points denoting the distance from them to which the molecular forces are operative. If the substance to the left of AB is air, the potential of Q is less than that of P, and surface tension results. If, on the other hand, this second substance is a solid, Q may be either at a greater or at a less potential than P. Hence, —

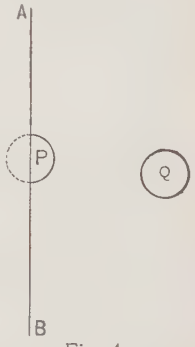


Fig. 4.

"If two small grains of clay, suspended in water, come close together, they may be attracted to each other or not, according to the potential of the water particles on the surface of the clay. If the potential of the surface particle is less than that of the particle in the interior of the mass of liquid, there will be surface tension, and the two grains will come together and be held with some force, as their close contact will diminish the number of surface particles in the liquid. If, on the other hand, the potential of the particle on the surface of the liquid is greater than that of the particle in the interior of the mass, the water surface around the grains will tend to enlarge, as there will be greater attraction for the particles there than in the interior of the mass of liquid, and the grains of clay will not come together, and will even be held apart, as their close contact would diminish the number of surface particles in the liquid around them."

K. Fuchs[2] has stated this last point very clearly and more generally : —

(1) If the molecules of the liquid are attracted more strongly by those of the solid than they are by other molecules of the liquid,

[1] U. S. Weather Bureau Bull. 4, 1892, pp. 19–20. The author states that the theory was suggested by Lord Rayleigh's article in the Phil. Mag., November and December, 1890, and also acknowledges advice and suggestions from Dr. A. L. Kimball. Notes of these hints, as well as correspondence with other scientific men, have been lent to the present writer, who acknowledges his own indebtedness thereto.

[2] Exner's Rep., XXV., pp. 735–742.

or than the molecules of solid attract one another, the potential energy will be a minimum, when each particle of solid is surrounded by a shell of liquid of the thickness of the radius of molecular force. The two particles will then repel each other if brought closer together than within twice this distance.

(2) If either of the forces, solid-solid or liquid-liquid, is greater than the force solid-liquid, the potential energy will be least when the two particles are approached as closely as possible. They will then attract.

These theories, as well as the treatment about to be given, require that the particles influenced be not very great compared with what is usually called "the sphere of molecular force." The radius of the latter is, according to Quincke, 0.000005 cm. The diameters of the clay particles are, according to Whitney, between 0.0005 and 0.00001 cm., *i.e.* from 100 times to twice the radius of attraction. According to Barus and Brewer they are ultra-microscopic, and the former considers 0.000005 a fair value, *i.e.* the same as the radius in question. Noting the dependence of the theory on a size of particles not much exceeding these values, we will now seek to pass from the general conception of a diminution in Potential Energy by a change in the relative position of the particles to the actual forces by which such change is brought about. For simplicity we limit our attention to two particles.

§ 18. Let the particles be rigid, homogeneous spheres, and let us assume the liquid about them homogeneous, and of the same density within the range of molecular forces. We will consider the effect of the solid on a unit volume of liquid at P, whose sphere of molecular action impinges on both spheres. The unit volume must, of course, be taken extremely minute.

(Fig. 5.) Let ABC and $A'B'C'$ be the sections of the two solid particles by a plane through their centers and through P. Let the circles $EFE'F'$ and $LMNS$ be drawn on P as a center, and cutting ABC and $A'B'C'$. They enclose a section of a spherical shell, of which P is the center. Draw the arcs EF and $E'F'$ symmetrical with BC and $B'C'$ as regards P. Then the resultant of the attraction of the spherical shell upon a small unit volume of liquid at P is made up of the attractions of several

pairs of equal volumes symmetrically situated as regards P, as follows:—

(1) $F'S'L'G'$ and $EMND$, whose resultant is zero, for they are both composed of solid, and are directly opposed to one another.

(2) $D'N'LG$ and $E'M'SF$, whose resultant is also zero, since both are liquid.

(3) $GLME$ and $G'L'M'E'$. For every element of one of these there is one in the other precisely similarly situated as regards P, but the one element composed of solid, the other of liquid. Therefore, if B be the attraction of a unit volume of the given

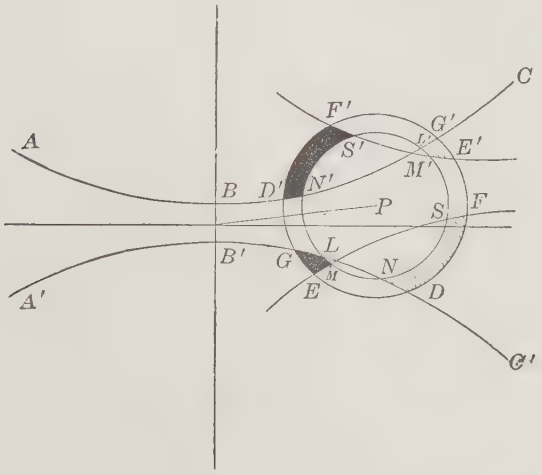


Fig. 5.

solid for one of the given liquid, at unit distance, and C the similar coefficient between unit volumes of liquid, the resultant of the two segments will be $(B-C)$ into an integral taken over either of the two, the force being taken positive when towards the solid.

(4) Similarly, the resultant of $D'N'S'F'$ and $DNSF$ will be $(B-C)$ into an integral taken over either of these segments.

Hence the resultant of the whole shell will be proportional to $(B-C)$. Taking the sum of all such shells which cut both solids, we get the total force upon the element P due to the presence of the two particles. Hence if a=radius of solid spheres; $e=BB'$, the distance between them; n=the distance of P from O, the

middle point of BB'; and ϕ the angle POB, then the force on unit volume at P is

$$p = (B - C)\, F(a, e, \phi, \text{and } r). \tag{1}$$

Considering the liquid between the spheres, each shell of liquid of radius r about O produces a pressure on all the liquid within it due to the force p, and hence on the two particles, tending to force them apart. Therefore resolving p along PO and integrating[1] throughout the liquid between them, we get the force Φ tending to separate the particles: —

$$\Phi = (B - C)\, F'(a, e). \tag{2}$$

The actual evaluation of F' without a knowledge of the law of variation of molecular attraction with the distance would, of course, be impossible. Even under the assumption that the law is that of the inverse fourth power, the writer has found it far from simple. The variation of the density, and probably the concentration of a salt solution near a solid surface, make it unlikely that B and C are accurately constant throughout the integration; but, while noting this assumption, we may take the above form as an approximation to the force introduced by the pressure of the liquid in trying to form a complete shell about each particle.

§ 19. The distance between the spheres is further affected by the attraction between the spheres themselves. Denoting by (ss) the coefficient of attraction between *unit masses* of the given solid, at unit distance, this force will be

$$\Psi = (ss) n^2 F''(a, e), \tag{3}$$

where n is the density of the solid. Φ and Ψ, in the absence of electrical forces, may be assumed to be the only ones acting, and therefore the force *holding the particles together* is

$$R = (ss) n^2 F''(a, e) - (B - C) F'(a, e). \tag{4}$$

§ 20. The coefficient $(B - C)$ is the only thing that changes in the value of this force when nothing is changed but the composi-

[1] This part of the process has since been found outlined by Barus and Schneider, Zeit. Phys. Chem. III. 3, 1891.

tion of the liquid. For a change in the latter, R increases as $(B-C)$ decreases. Since increased flocculation means an increase of the force holding the particles together, *i.e.* of R, increased flocculation means that $(B-C)$ has decreased. Hence, to explain the facts of flocculation, —

(1) $B-C$ must decrease when a trace of flocculent substance is added to pure water. Calling σ the mass of salt added to unit volume, —

$$\left[\frac{d(B-C)}{d\sigma}\right]_{\sigma=0}$$

must be negative for such substances.

(2) This quantity must be positive for alkalies such as KOH.

(3) Increase of concentration in the case of flocculent substances produces increased flocculation. In the case of alkalies it reverses the effect of a trace, and also causes strong flocculation. Therefore, $\frac{d^2(B-C)}{d\sigma^2}$ is negative for all substances.

The next step is then to find B and C in terms of σ.

§ 21. C is the measure of the attraction of two unit volumes of liquid. In a salt solution it is probably slightly greater near the solid than in a portion of the same solution further away,[1] and differs still more from the value at an air surface. It is therefore only roughly proportional to the surface tension as usually measured.

On the value of B there is no experimental evidence, so far as I am aware. It is, however, instructive to try the result of a simple hypothesis as to the form of both B and C. Let us start with pure water and denote by (ww) the mutual attraction of two unit *masses* of water. Thus for a density ρ of water we can write $C=\rho^2(ww)$. So, if (sw) denote the attraction between a unit mass of the water and a unit mass of solid, and n is the density of the latter, $B=n\rho(sw)$.

$$\therefore B-C=\rho\{n(sw)-\rho(ww)\}, \tag{5}$$

$$\frac{d(B-C)}{d\rho}=n(sw)-2\,\rho(ww). \tag{6}$$

[1] J. J. Thomson's Applications of Dynamics to Phys. and Chem., p. 191.

Let us see from this equation what the effect of heating on flocculation teaches us as to the relative values of (ww) and (sw). Barus shows[1] that rise of temperature in pure water produces flocculation. Since ρ, the density of the water, decreases with heating, the condition that $B-C$ also decreases is that $n(sw)-2\rho(ww)$ shall be positive, *i.e.* $n(sw)>2\rho(ww)$. Since n for an individual clay particle is not far from 2.6, we have in round numbers, ρ being about 1

$$(sw)>\frac{(ww)}{1.3} \text{ or } \tfrac{3}{4}(ww). \tag{7}$$

Extending the above formulæ for B and C by the simple hypothesis that the effect of salt in very dilute solution is merely additive, we have for B in such a dilute solution,

$$B=\rho' n(sw)+\sigma n(st), \tag{8}$$

where (st) is the attraction of unit masses of salt and solid, and σ the mass of salt in unit volume. Similarly formed constants give for C,

$$C=\rho'^2(ww)+2\sigma\rho'(wt)+\sigma^2(tt), \tag{9}$$

where (tt) is the attraction between two unit masses of the salt, and (wt) between water and salt.

§ 22. A formula analogous to the above has since been found to be used by Volkmann[2] to express the surface tension of a mixture, densities being replaced by the volumes of the solutions mixed, and the constants (ww), etc., by their surface tensions independently. He mentions previous use of it by Poisson, and also quotes from O. E. Meyer[3] a similar expression for the viscosity of a mixture. Sutherland[4] finds a much more complicated expression to agree best with experimental results on surface tension and compressibility, the law of the inverse fourth power being assumed, and also a number of other conditions. As nearly as possible in the present notation his formula is

$$C=\bar{\rho}^2\cdot\frac{(1+n)(ww)(tt)}{(tt)+n(ww)}, \tag{10}$$

[1] Bull. 36 U. S. Geol. Surv., p. 23.
[2] Wied. Ann., Vol. XVI., p. 321, and Vol. XVII., p. 384.
[3] Pogg. Ann. 113, p. 405, 1861.
[4] Phil. Mag., March, 1893.

where $\bar{\rho}$ is the density of the liquid as a whole, and n the number of salt molecules to one of water. The complexity of this formula may very probably be due, at least in the case of surface tension, to the fact that while the densities and concentration of the solution are those in the interior, the value of C concerned is that for volumes near an air surface, where both the former quantities might be very much modified. The mathematical work, however, of connecting such a constant with experimental results is very complicated, and in the present state of science involves so many assumptions as to be inconclusive, and it seems, therefore, hardly advisable to abandon the simpler expression found in § 21 for the above, at least for the present purpose.

§ 23. The value of ρ', *i.e.* the weight of water in unit volume of the solution after the salt has been put into an amount σ per unit of volume, may be denoted closely enough for present purposes (very dilute solutions) by $\rho' = \rho - \alpha\sigma$, where α is a small constant calculated from densities of salt solutions. A few values[1] are given below:—

Flocculent substances,

NaCl and KCl, $\alpha = 0.3$; HCl, $\alpha = 0.4$.

Substances which prevent flocculation,

KOH, $\alpha = 0.07$; Borax, $\alpha = 0.8$; NH_4OH, $\alpha = 1.1$.

Introducing this value of ρ' in our values for B and C,

$$B = (\rho - \alpha\sigma)n(sw) + \sigma n(st) = \rho n(sw) + \sigma n\{(st) - \alpha(sw)\}. \quad (11)$$

$$C = \rho^2(ww) + 2\rho\sigma\{(wt) - \alpha(ww)\} + \sigma^2\{(tt) - 2\alpha(wt) + \alpha^2(ww)\}. \quad (12)$$

$$B - C = \rho n(sw) - \rho^2(ww) + \sigma[n\{(st) - \alpha(sw)\} - 2\rho\{(wt) - \alpha(ww)\}] - \sigma^2\{(tt) - 2\alpha(wt) + \alpha^2(ww)\}. \quad (13)$$

§ 24. This equation connects B and C with the density of salt in the solution, and in order to find the effect of an addition of salt on the force holding the particles together, we differentiate with regard to σ:—

$$\frac{d(B-C)}{d\sigma} = n\{(st) - \alpha(sw)\} - 2\rho\{(wt) - \alpha(ww)\} - 2\sigma\{(tt) - 2\alpha(wt) + \alpha^2(ww)\}. \quad (14)$$

[1] Landholt and Börnstein's Tabellen; Röntgen & Schneider, Wied. Ann.

By now putting $\sigma=0$, we get the effect on flocculation of the first trace of salt: —

$$\left[\frac{d(B-C)}{d\sigma}\right]_{\sigma=0} = n(st) + 2\,\rho\alpha(ww) - 2\,\rho(wt) - n\alpha(sw). \qquad (15)$$

But it was shown in § 21, that in order to account for flocculation by rise of temperature,

$$(sw) > \frac{2\,\rho}{n}(ww).$$

∴ Assuming $\rho=1$, and n, for clay $=2.6$,

$$\left[\frac{d(B-C)}{d\sigma}\right]_{\sigma=0} = 2.6(st) - 2(wt) - \alpha \times \text{a positive quantity.} \qquad (16)$$

If the right hand member is negative, the first trace of salt causes flocculation; *i.e.* salts where $(st) < \frac{3}{4}(wt)$, or which attract the given clay only three-quarters as strongly as they do water, belong to the flocculent class. On the other hand, if (st) is considerably greater than (wt), $B-C$ will increase upon the addition of the first trace of salt, and the latter belongs to the class like KOH, which prevents flocculation when only a trace is present. The value of α here makes a great difference, and KOH and borax, with small values of this constant, need attract the solid very little more than three-quarters as much as they do water; while ammonia, which very much reduces the water in unit volume, must have a very much larger relative attraction for the solid, or it would cause flocculation instead of preventing it.

§ 25. In order to find the conditions under which continued additions of salt always tend to increase the tendency to flocculation, even where the first trace has the opposite effect, we must apply the condition (3) of § 20; *i.e.* $\frac{d^2(B-C)}{d\sigma^2}$ is always negative. Hence, differentiating again in (14),

$$\frac{d^2(B-C)}{d\sigma^2} = -2\{(tt) - 2\,\alpha(wt) + \alpha^2(ww)\}, \qquad (17)$$

so that the quantity in brackets must be positive for all substances tried, *i.e.* $(tt) + \alpha^2(ww) > 2\,\alpha(wt)$.

For KOH, where $\alpha = 0.07$, α^2 may be neglected, and in order to

account for the production of flocculation by an excess of KOH we need only suppose that $(tt) > 0.14(wt)$; that is, a comparatively weak attraction of KOH for itself as compared with its attraction for water is sufficient.

For NH_4OH, on the other hand, $\alpha = 1.1$, and the condition becomes $(tt) + 1.2(ww) > 2.2(wt)$, which means that the inter-attraction of ammonia and water is weak compared to the attraction of each for itself.

Similarly for flocculating substances, whose effect on flocculation increases *a fortiori* with the quantity present, the same equation holds, and, for example, in the case of NaCl, where $\alpha = 0.3$, becomes

$$(tt) + 0.09(ww) > 0.6\ (wt)\ ;$$

i.e. the lowest assignable value for the attraction of unit masses of salt for one another, must be not far from $\frac{1}{2}$ of the attraction between common salt and water.

§ 26. The last paragraph showed how from experiments on flocculation, assuming the present theory, rough relative values may be deduced for the coefficients of attraction between various soluble substances and water. Similarly, from the section before we get relative values of the coefficients between salts and water on the one hand, and salts and solids on the other. The solid specially referred to in the instances given is such clay as gives the results obtained by most experimenters on flocculation. With different solids the effects in flocculation might be very different, since n, the density, as well as the constants (ss), (st), and (sw), in the above equations would vary. For instance, Brewer[1] experimented with Hartford clay, and himself remarks upon the almost exactly opposite results obtained by him from those of most other experimenters. He found that even so small a trace as 0.0008 gr. of KOH per cu. cm. aided precipitation; while, on the other hand, a very dilute mixture of nitric and hydrochloric acid (one part to several thousand of water) held the clay in suspension. In such clay the attraction between the clay and KOH would be less than its attraction for the acids instead of greater. On the other hand, the experiments of the first part of the present paper showed that

[1] Memoir, National Academy of Sciences, February, 1883.

glass has about the same relative values of the coefficients as the more usual clays.

The results of § 25 are entirely independent of the solid, and concern only water and the substance dissolved therein.

§ 38. The most useful outcome of the above discussion seems to be the means afforded of comparing the consequences of the theory given, as stated in the results of the last sections, with our general information concerning the various substances. To this end they are summarized below in round numbers, the forces being measured between unit masses at unit distance. From the clay referred to is to be expressly excluded such clay as the Hartford clay of Brewer, which seems to be exceptional; while, on the other hand, about the same properties may be set down to glass as are here ascribed to clay.

(1) The force between clay and water is greater than three-quarters the attraction of water for itself.

(2) The attraction of ammonia for clay must considerably exceed that of ammonia for water. KOH and the substances of which it is typical must have an attraction for clay *greater* than three-fourths that between the salt and water, while flocculating substances such as NaCl must have an attraction for clay *less* than three-fourths that for water.

(3) The attraction of NaCl for itself must be at least as great as three-quarters its attraction for water. The attraction of KOH for itself need only be from one-tenth to two-tenths its attraction for water. The attraction of ammonia for itself, and of water for itself, must be at least as great as their mutual attraction; or at least if the attraction of ammonia for itself is not as great as its attraction for water, the deficiency must be made up by a very strong attraction of water for itself (relatively to the two other coefficients).

The relative attraction of KOH and salt for water in (3) is interesting in view of the heat evolved when KOH is dissolved, and other parallels between the above and well-known properties of the various substances will readily occur to the reader.

§ 28. The subject of flocculation is one of sufficient practical interest in connection with its effect upon soil texture, as well as

its action in sedimentation, to repay a direct study. Data are at present given for the most part only incidentally in describing experiments upon the rate of settling of sediments and precipitates. Its importance in this latter phenomenon has even to a large extent been overlooked, and the effect of traces of salts, ascribed to changes in the viscosity of the liquid and a variety of other causes, many of which are undoubtedly active enough to prevent the rate of settling from being more than a rough guide to the state of flocculation. Direct experiments might be made with a microscope, or perhaps by the colors of light transmitted through the suspended particles, and for merely scientific purposes they should be made on other substances besides soils. The writer proposes at once to try to extend the experiments of Part I. of the present article to a much greater range of salts, and also, if possible, by a modification of the apparatus, to obtain curves connecting the thickness of the liquid film intervening between the glass surfaces with the concentration of the solution.

Quantitative values of the constants in the theory just given could hardly be hoped for from experiments on flocculation, nor could the law of force be determined from them. The writer believes, however, that a process similar to the one here given, applied as rigorously as possible to the calculation of surface tensions of salt solutions and mixtures, would repay the very considerable labor of developing it. He has himself made a beginning, assuming the law of the inverse fourth power, but endeavoring to calculate the density in the surface film instead of assuming a probable value for it.

Note.

Since the work given in the above pages was done, there has appeared in the *Philosophical Magazine*, March, 1894, an article by Dr. G. Gore, in which he attacks in a different manner the relative attractions of various solids and salts. His method has the very great advantage of yielding quantitative results, but of a kind not readily interpreted. The experiments measure the rise in temperature of pure water and of various salt solutions when certain solids in the form of powder are poured

into them. The heat given to the liquid comes from the combination of several changes of energy.

(1) Heat absorbed by the separation of the solid particles from one another.

(2) Heat liberated by the liquid wetting the particles, *i.e.* replacing air in their surface films. This is the energy Dr. Gore believes he has measured.

(3) Further change of energy as the powder packs together at the bottom of the vessel and the liquid is squeezed out.

The combined effect of (1) and (3) is the change in the potential energy of the solid due to the change in compactness between a dry and a wet powder, which it does not seem proper to neglect. We consequently find a marked difference between his results and the phenomena of flocculation. In the latter pure clay is held in a more separated condition in pure water than in any solutions except extremely dilute ones of certain alkalies. Since Dr. Gore's solutions are 10 per cent, the heat liberated by the wetting of clay by pure water should be greater than when it is wet by any of his solutions. We find, on the contrary, that in the case of both silica and alumina the heat given out in wetting by dropping them into pure water has a medium value exceeded in the case of a number of solutions with each of the two solids. We should not perhaps expect pure silica and alumina to give exactly the same results as clay, but in view of the fact that such strong solutions have been found to flocculate a wide range of materials when in suspension, the discrepancy seems more likely to lie in the cause given above.